Measurement of Contemporary and Fossil Carbon Contents of PM$_{2.5}$ Aerosols: Results from Turtleback Dome, Yosemite National Park

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The impact of aerosol particulate matter of mean mass aerodynamic diameter ≤2.5 μm (PM$_{2.5}$ aerosols) on health, visibility, and compliance with the U.S. EPA's regional haze regulations is a growing concern. Techniques that can help better characterize particulate matter are required to better understand the constituents, causes, and sources of PM$_{2.5}$ aerosols. Measurement of the ^{14}C/C ratio of the PM$_{2.5}$ aerosols, the absence of ^{14}C in fossil carbon materials, and the known ^{14}C/C levels in contemporary carbon materials allow the use of a two-component model to derive contemporary and fossil carbon contents of the particulate matter. Such data can be used to estimate the relative contributions of fossil fuels and biogenic aerosols to the total aerosol loading. Here, the methodology for performing such an assessment using total suspended particulate hi-vol aerosol samplers to collect PM$_{2.5}$ aerosols on quartz fiber filters and the technique of accelerator mass spectrometry to measure ^{14}C/C ratios is presented and illustrated using PM$_{2.5}$ aerosols collected at Yosemite National Park.

Introduction

On July 18, 1997, the U.S. Environmental Protection Agency (EPA) issued revised National Ambient Air Quality Standards (NAAQS) particulate matter (PM) (*1*). In actions for PM$_{2.5}$ aerosols (particles with mean mass aerodynamic diameter ≤2.5 μm) NAAQS, the EPA has determined that visibility impairment due to regional haze is a PM$_{2.5}$ effect of concern (*2*). Consequently, the impact of PM$_{2.5}$ aerosols on health, visibility, and compliance with the EPA's regional haze regulations is a growing concern. Techniques that can help better characterize particulate matter are required to better understand the causes and sources of PM$_{2.5}$ aerosols.

Radiocarbon (^{14}C) is a naturally occurring radioisotope, produced in the atmosphere by cosmic ray interaction with ^{14}N. It oxidizes to CO$_2$ and enters the food chain through plant photosynthesis so that all living things are intrinsically labeled with a characteristic ^{14}C/C ratio. Atmospheric nuclear testing produced large additional quantities of ^{14}C in the late 1950s and early 1960s: the radiocarbon content of the atmosphere doubled in the Northern Hemisphere between 1955 and 1963 (*3*). Since the almost complete cessation of atmospheric testing in 1964, atmospheric ^{14}C levels have been declining as this excess is mixed into the biosphere. The present atmospheric ^{14}C/C ratio, expressed in terms of the

"Modern" radiocarbon nomenclature (*4*), is 109% Modern Carbon (pMC) (*5*) or 1.09 times Modern (fraction Modern). The carbon content of materials that possess ^{14}C/C ratios that are similar to the present atmospheric ^{14}C/C level is often described as contemporary carbon, and such materials are often referred to as containing contemporary radiocarbon levels.

Contemporary carbon in aerosol particulate matter is primarily biogenic in origin arising from the growth, natural biologic processes, destruction, and anthropogenic use of trees and plants. Trees and other perennial plants contain a year-by-year record of atmospheric ^{14}C in the radiocarbon content of their wood, leaves, etc. Leaves and small twigs have ^{14}C/C ratios at or close to the present 1.09 fraction Modern. The interiors of larger branches—wood from closer to the time of atmospheric testing—contain more ^{14}C. Inner rings of old trees dating from before atmospheric nuclear testing have ^{14}C levels below Modern.

Thus, carbon-containing aerosols derived from trees and plants, unless they come from greater than 45-year-old wood, will tend to contain radiocarbon levels at or above Modern. However, the exact levels will depend on the source material and may even vary with time in the case of sources such as wood smoke arising from fire burning into large branches or logs spanning significant numbers of years of different ^{14}C concentration.

In contrast, fossil fuel-derived materials are made from carbon that was sequestered underground for periods that were very long as compared to the 5730-yr half-life of ^{14}C. Hence oil, coal, and materials and particles derived from these feedstocks are radiocarbon-free. The carbon content of materials that possess no ^{14}C is often described as fossil carbon, and such materials are often referred to as fossil carbon material.

Other sources of carbon in the particulate matter can arise from carbonate dust and soil organics. Carbonates will provide an additional source of material that frequently contains no ^{14}C and can thus have a ^{14}C/C ratio that is identical to that of fossil carbon material, while radiocarbon activities of surface soil organics are typically close to or lower than those of contemporary carbon materials (*6*).

In principle, the absence of ^{14}C in fossil carbon materials and the known ^{14}C/C levels in contemporary carbon materials provides a method to determine contemporary biogenic and fossil carbon contents of PM$_{2.5}$ aerosols if the ^{14}C/C ratio of the PM$_{2.5}$ aerosols can be measured and if contributions from soil organics and carbonates are small. Here, the methodology for performing such an assessment using aerosol samplers to collect PM$_{2.5}$ aerosols on quartz fiber filters and the technique of accelerator mass spectrometry (AMS) to measure ^{14}C/C ratios is presented and illustrated using PM$_{2.5}$ aerosols collected at Turtleback Dome, Yosemite National Park, during the summer of 2002.

Experimental Section

Sample Collection. Aerosol particulate matter was sampled at Turtleback Dome, Yosemite National Park, at an elevation of 1605 m above sea level. Samples were collected using a Thermo Anderson total suspended particulate (TSP) hi-vol sampler with a SA-230-F impactor plate. The sampler was operated at a volumetric flow of 1130 L/min to yield a PM$_{2.5}$ sample on a 20 × 25 cm^2 quartz fiber filter (Gellman QM-A). One quartz fiber filter was used per sampling period, and all quartz filters were prefired by baking at 600 °C for 12 h and stored in sealed plastic bags prior to use. One slotted glass fiber substrate was installed in the hi-vol impactor head per

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sampling period to collect particles greater than 2.5 μm. The glass fiber substrates were stored in sealed plastic bags prior to use, were only used for sizing, and were discarded following sampling.

PM$_{2.5}$ aerosols were sampled daily from approximately 8:00 am to 8:00 pm PST from July 14 through September 3, 2002. Over the course of the collection periods, the prevailing wind direction was from the west-southwest corresponding to upslope flow from the San Joaquin Valley below Yosemite National Park. In many instances 12-h sampling was utilized on the same quartz filter for three consecutive days for a total sampling of 36 h. However, when anticipated climate conditions suggested that PM$_{2.5}$ levels might be substantially higher than average, quartz filters were changed daily or once every two days.

Thirteen quartz filters including three at beginning, three toward the middle, and two at the end of the study acted as vehicle controls. Each of these filters was placed in the sampler for 10 min when it was not operating.

Following deployment, quartz filters were immediately placed in new resealable plastic bags. The bagged filters were stored flat and unfolded in a cool dry, dark environment within a plastic container prior to shipment to Lawrence Livermore National Laboratory (LLNL) for analysis.

Sample Preparation. At LLNL, areal samples of size 25 cm^2 (5 × 5 cm) were cut with a knife from the central region of each quartz filter. Each sample was directly combusted in a vacuum at 900 °C with CuO oxidizer in a sealed quartz tube. CO$_2$ from the combustion was cryogenically isolated from other combustion products and measured manometrically before conversion to graphite by hydrogen reduction using a cobalt catalyst (7, 8).

^{14}C/C ratios for the graphite samples were measured by AMS at LLNL (9). The data were reported as a fraction of the Modern radiocarbon standard (fraction Modern or FM) (4). Measurements of CO$_2$ obtained from combustion of duplicate areal samples by conventional mass spectrometry produced δ^{13}C values varying between −22 and −27‰ averaging −25 ± 1‰. The average δ^{13}C value was assumed for all PM$_{2.5}$ aerosol samples in order to correct the radiocarbon measurements for isotopic fractionation effects.

Duplicate radiocarbon analyses were performed on eight randomly selected PM$_{2.5}$ aerosol-laden filters. For the replicate analysis, another square 25 cm^2 region toward the edge of the filter was analyzed.

Data Reduction and Analysis. The geologic and atmospheric factors present during the sampling periods suggested that it was justifiable to consider the carbon content of the PM$_{2.5}$ aerosols as a two-component mixture of contemporary biogenic and fossil carbon (see Results and Discussion). For aerosol particulate matter whose carbon content is dominated by contemporary and/or fossil carbon, measurement of the ^{14}C/C ratio and knowledge of the ^{14}C/C levels in contemporary carbon affords use of a simple two-component method to determine the contemporary and fossil carbon contents. If R_a is the ^{14}C/C ratio of the PM$_{2.5}$ aerosol sample and R_c is the ^{14}C/C ratio of the contemporary component, then the fraction F_c of the carbon on the filter that is derived from contemporary carbon is given by

$$F_c = R_a/R_c \qquad (1)$$

because all of the radiocarbon must come from the contemporary fraction. Over the period from 1997 to 2002, the fraction Modern of contemporary samples slowly decreased from 1.12 to 1.08 (5, 10). Hence, for this study, R_c (the ^{14}C/C ratio of the contemporary component) was assumed to be 1.10 ± 0.02.

To account for any endogenous carbon on the quartz filters prior to sampling PM$_{2.5}$ aerosols, measured ^{14}C/C ratios

were corrected using the mixing equation:

$$R_a = R_m L_m/(L_m - L_b) - R_b L_b/(L_m - L_b) \qquad (2)$$

where R_a is the ^{14}C/C ratio of the PM$_{2.5}$ aerosol, R_m is the measured ^{14}C/C ratio of the PM$_{2.5}$ aerosol-laden filter, L_m is the carbon mass of the analyzed region of the filter, L_b is the carbon mass on the analyzed region of a vehicle control filter, R_b is the ^{14}C/C ratio of a vehicle control filter, and $L_m - L_b$ is the PM$_{2.5}$ aerosol carbon mass. R_m, L_m, and L_b have Gaussian-type errors, so uncertainties in R_a in eq 2 were derived from those in the measured quantities using appropriate standard error propagation relationships that have been previously described (11, 12).

Contemporary and fossil carbon masses (μg) in the PM$_{2.5}$ aerosol were derived using eq 1 with R_a determined by eq 2. Total, contemporary, and fossil carbon masses were converted to PM$_{2.5}$ aerosol concentrations (units of μg/m^3) using the volume of air sampled for each sampling period, the area of the quartz filter analyzed via AMS, and the total area of the quartz fiber filter through which the sampled air was drawn.

Results and Discussion

The average (mean ± standard deviation) values of carbon mass and FM obtained from the 13 vehicle control filters were 0.053 ± 0.013 mg and 0.7919 ± 0.1030, respectively. These values were used to correct analyses of PM$_{2.5}$ aerosol-laden filter samples for contributions from endogenous filter carbon.

Replicate analyses of the eight randomly selected PM$_{2.5}$ aerosol-laden filters revealed consistency in both mass of carbon and associated FM to within measurement uncertainties corresponding to 1σ values of 0.02 mg for mass and 0.005 for FM for each filter. This suggests that the sampled area of 5 × 5 cm yields carbon loadings and FMs that are representative of the whole filter.

Table 1 shows the total carbon content and associated FM of the PM$_{2.5}$ aerosol from the sampled area of each laden filter. The similarity of the uncertainties in aerosol carbon mass values in Table 1 arises as the uncertainty associated with the manometry measurement, which is independent of mass, dominates other uncertainties. Contemporary and fossil carbon contents of the aerosols derived from the data in Table 1 using the two-component model described in eq 1 are plotted against total carbon content in Figure 1.

Use of the two-component model yields a first-order answer to derive fossil and contemporary biogenic carbon contents and assumes that contributions from nonfossil and noncontemporary sources of carbon during the sampling periods were nonexistent or small. It may not be valid to use the model if other sources of carbon contribute significantly to the aerosol particulate matter, as multicomponent mixtures must then be considered. For instance, the presence of significant quantities of carbonates in particulate matter can lead the model to overestimate the fossil carbon content while the presence of soil organics can lead the model to incorrectly estimate both the contemporary biogenic and the fossil carbon contents. However, the use of an unconstrained multicomponent model is often impractical, as all source terms are not known. Despite the caveat that other source terms may be present, use of a two-component model provides a convenient technique to derive contemporary and fossil carbon contents of the particulate matter.

For the summer of 2002 at Turtleback Dome, there is ample data that justify application of the two-component model to the data in Table 1 (13−15). These studies all indicated that contributions from carbonates and soil organics were minimal. Part of the reason for this maybe that Turtleback Dome is composed of granite and that the

TABLE 1. Carbon Content and the Associated Fraction Modern (FM) of PM$_{2.5}$ Aerosols Obtained from the Sampled Area of Each Aerosol-Laden Filter

sample[a]	corrected C mass (mg)[b]	±	corrected FM[b]	±
7/14−16/02	0.557	0.023	0.8460	0.0524
7/17−19/02	0.507	0.023	0.8139	0.0558
7/20−21/02	0.437	0.023	0.8008	0.0639
7/22−24/02	0.627	0.023	0.8838	0.0481
7/25−27/02	0.627	0.023	0.8821	0.0480
7/28/02	0.357	0.023	0.8965	0.0850
7/29/02	0.297	0.023	0.9483	0.1066
7/30/02	0.317	0.023	0.9725	0.1019
7/31−8/2/02	0.657	0.023	0.9513	0.0487
8/3−5/02	0.787	0.023	0.9465	0.0406
8/6−7/02	0.357	0.023	0.9265	0.0873
8/8−9/02	0.527	0.023	0.9596	0.0614
8/10/02	0.347	0.023	0.9665	0.0928
8/11−13/02	0.867	0.023	0.9736	0.0378
8/14/02	0.457	0.023	1.0316	0.0747
8/15/02	0.477	0.023	1.0471	0.0726
8/16−18/02	0.907	0.023	1.0473	0.0388
8/19−21/02	0.907	0.023	1.0315	0.0382
8/22−24/02	0.687	0.023	0.9410	0.0463
8/25−27/02	0.797	0.023	0.9751	0.0410
8/28−30/02	0.717	0.023	0.9351	0.0440
8/31−9/1/02	0.327	0.023	0.9348	0.0958
9/2−3/02	0.227	0.023	0.9361	0.1377

[a] Sample description refers to the date or dates of sampling for a filter. [b] Carbon masses and fraction Moderns have been corrected using eq 2 for contributions from endogenous carbon on the vehicle control filters.
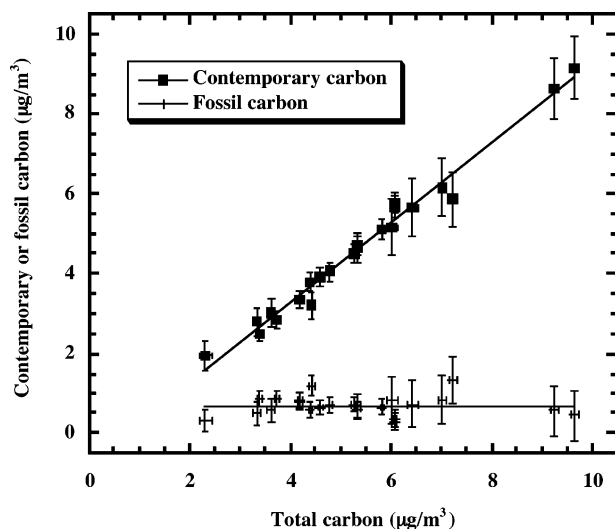

FIGURE 1. Graph of contemporary carbon (black squares) and fossil carbon (crosses) concentration vs total carbon concentration for PM$_{2.5}$ aerosols collected at Turtleback Dome from July 14 through September 3, 2002. The solid lines are linear least-squares fits to the data. The least-squares fit to the contemporary carbon data has a gradient of 0.9997 and a coefficient of correlation of 0.99. The least-squares fit to the fossil carbon data has a gradient of −0.00007.

sampler was installed on bedrock at the summit with little soil present in the vicinity of the sampler. In addition, visibility at the sampling site was periodically impaired due to significant contributions from smoke derived from wild fires for several periods in the study (13, 14). PM$_{2.5}$ aerosol organic carbon contents at Turtleback Dome during the summer of 2002 are consistent with significant smoke contributions periodically impairing visibility. PM$_{2.5}$ aerosol organic carbon contents were substantially higher than the historical average of ∼3 μg/m^3 and varied between 2 and 10 μg/m^3, averaging

∼5.5 μg/m^3, while total carbon contents averaged ∼6 μg/m^3 (13, 14). These geologic and atmospheric factors suggest that contributions from nonfossil and noncontemporary sources of carbon during the sampling periods were minimal and that it is justifiable to consider the carbon contents of the PM$_{2.5}$ aerosols as a two-component mixture of contemporary and fossil carbon.

The data in Figure 1 reveal that the fossil carbon concentration appears to be constant at ∼0.7 ± 0.1 μg/m^3 and is independent of the total carbon content of the PM$_{2.5}$ aerosol. Conversely, the contemporary carbon content varies in direct proportion to the total carbon content of the PM$_{2.5}$ aerosols with a gradient of 0.9997, an intercept of −0.7, and a coefficient of correlation of 0.99. This implies that variation in the total carbon loading at Turtleback Dome arises solely from variation in the contemporary carbon loading of the PM$_{2.5}$ aerosols.

Several inferences can be drawn from the two-component modeling. Because the aerosol PM$_{2.5}$ fossil carbon content was effectively constant during the study period and typically much smaller than the contemporary carbon content, it is unlikely that fossil fuel emissions contributed significantly to periods of impaired visibility at Yosemite during the summer of 2002. These data are consistent with organic speciation studies conducted concurrently at Turtleback Dome with the study reported. The organic speciation studies showed that vehicular emission tracers (hopanes and steranes) were detected at low concentrations, suggesting less than 10% contribution to average particulate organic mater (15).

In addition, since contemporary carbon in aerosol particulate matter is primarily biogenic in origin, the data in Figure 1 suggest that the majority of PM$_{2.5}$ aerosol carbon at Yosemite during the summer of 2002 was biogenic in origin. The large variability in PM$_{2.5}$ aerosol contemporary carbon content observed in Figure 1 likely arises from significant variations in a biogenic source or sources. As visibility at the sampling site was periodically impaired due to significant contributions from smoke for several periods in the study (13, 14), a plausible biogenic source for at least some of the variability is smoke from wild fires. This finding is consistent with organic speciation studies and organic and black carbon studies conducted concurrently with the study reported here (14, 15). Concentrations of pinene oxidation products, including pinic and pinonic acids, were high accounting for several percent of total organic carbon on average and suggesting the contribution of secondary organic aerosol from biogenic sources (15). Certain periods, particularly during mid-August, showed a clear influence from wildfires, illustrated by high concentrations of wood smoke markers (resinacids, anhydrosugars, methoxyphenols) (15). The ratio of organic carbon to black carbon (OC/BC) was high throughout the sampling period (14, 15). Maximum OC/BC ratios occurred during relatively clear conditions when black carbon concentrations were low but organic carbon remained elevated, suggesting a contribution of biogenic carbon in addition to smoke. OC/BC ratios during the most severe haze were similar to values found in smoke plumes and much higher than those observed in polluted urban areas (14, 15).

The study shows that although, by itself, radiocarbon data has limited capability for identifying sources, it has significant potential and power to help distinguish sources and could be part of a method to improve the fingerprints of sources for receptor modeling. The method has an analysis cost of a few hundred dollars a sample. However, as only a portion of the sample is used for radiocarbon analysis, the remaining sample material could be used to obtain information (via elemental analysis, organic speciation studies, and organic and black carbon analyses) to help isolate sources.

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